Japanese Kokai Patent Application No. Hei 2[1990]-267137

Translated from Japanese by the McElroy Translation Company
800-531-9977 customerservice@mcelroytranslation.com

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. HEI 2[1990]-267137

Int. Cl.^{5}:	C 03 C 8/24 8/10
Sequence No. for Office Use:	6570-4G
Filing No.:	Hei 1[1989]-85770
Filing Date:	April 6, 1989
No. of Claims:	5 (Total of 6 pages)
Examination Request:	Not filed

SEALANT

Inventors:	Takashi Maekawa Hitachi Laboratories Hitachi Ltd. 4026 Kuji Hitachi, Ibaraki
	Takashi Naito Hitachi Laboratories Hitachi Ltd. 4026 Kuji Hitachi, Ibaraki
	Seiichi Yamada Hitachi Laboratories Hitachi Ltd. 4026 Kuji Hitachi, Ibaraki
	Kunihiro Maeda Hitachi Laboratories Hitachi Ltd. 4026 Kuji Hitachi, Ibaraki

Applicant: Hitachi Ltd.
4-6 Kandasurugatai
Chiyodaku, Tokyo

Agents: Hiroshi Nakamoto, patent attorney,
and 1 other

[There are no amendments to this patent]

Claims

1. Sealant comprising a mixture of V_2O_5-based low-melting glass powder and powder with low thermal expansion.

2. Sealant comprising a mixture of a low-melting glass powder from V_2O_5-based amorphous glass containing P_2O_5 and Sb_2O_3 and powder with low thermal expansion.

3. Sealant comprising a mixture of V_2O_5-based low-melting glass powder having distortion temperature (viscosity: 10^{11} P) below 400°C and thermal expansion coefficient below 90×10^{-7}/°C and powder with low thermal expansion.

4. Sealant comprising a mixture of V_2O_5-based low-melting glass powder and powder with low thermal expansion from one or more chosen from β-eucryptite, β-spodumene, cordierite, quartz glass, lead titanate, $NaZr_2(PO_4)_3$, $CaZr_2(PO_4)_3$, and $KZr_2(PO_4)_3$ and powder with low thermal expansion.

5. Ceramic package characterized by being sealed by a sealant comprising a mixture of V_2O_5-based low-melting glass powder and powder with low thermal expansion.

Detailed explanation of the invention

Industrial application field

The present invention concerns sealants capable of creating airtight seals at low temperature, especially low-temperature low-thermal-expansion sealants suitable for sealing LSI packages using low-thermal-expansion ceramics.

Prior art

Conventionally, in sealing Si semiconductors, etc., using packages, because it is necessary to inhibit thermal conduction to Si semiconductors, sealing at the lowest temperature possible is desired, and for maintaining airtightness of packages, sealants having good flowability and low thermal expansion comparable to that of the semiconductor are desired.

Up to now, for sealing ceramic LSI packages, as shown in Japanese Kokai Patent Application Nos. Sho 59[1984]-164649, Sho 60[1985]-27620, etc., sealants were developed by combining PbO-B_2O_5-based substrate glass with low-thermal-expansion material (filler).

With the sealants comprising substrate glass of mainly PbO, sealing at low temperature is possible. However, because of high thermal expansion of the substrate glass itself, there is a limit in making the thermal expansion low even when mixed with filler. Thus, for ceramic packages using such sealants, only aluminum packages can be used.

For improving the reliability of LSI packages, it is necessary for sealing packages using ceramics having thermal expansion properties comparable to those of Si semiconductors for reducing thermal stress exerted to Si semiconductors. Therefore, low thermal expansion of substrate glass itself is desired. As a result of various investigations of such substrate glass, we have discovered mainly V_2O_5-based glass has low softening temperature disclosed in Japanese Kokai Patent Application No. Sho 62[1987]-78128.

Problems to be solved by the invention

Conventional sealants based on mainly PbO-B_2O_3-based glass have high thermal expansion of the substrate glass; thus, using such sealants in sealing ceramic packages with a thermal expansion lower than that of alumina, e.g., packages using mullite, SiC, AlN, etc., as substrates is difficult.

Conventional sealants have some limitations when applied in ceramic packages. For example, in the case of the above alumina packages, due to the thermal expansion difference in the Si semiconductor, cracking may occur in the Si semiconductor. Furthermore, because substrate glass has PbO-B_2O_3 as the main component, the glass strength is low and thus is easily cracked even by a small impact; thus, airtightness cannot be maintained. Also, chemical durability is not sufficient, and in environmental tests such as moisture resistance, etc., satisfactory results cannot be obtained. Conventional PbO-B_2O_3 substrate glass has high reactivity toward fillers, and the sealant viscosity is high in sealing packages with reduced flowability, resulting in difficulties in low-temperature sealing.

Thus, with conventional sealants, improving LSI package reliability is difficult.

Namely, it is an object of the present invention to provide sealants most suitable for packages using low-thermal-expansion ceramic substrates having thermal expansion properties comparable to those of Si semiconductors, for enhancing the reliability of LSI packages.

Means to solve the problems

To achieve such objectives, in the present invention, sealants comprise a mixture of V_2O_5-based low-melting glass powder and powder with low thermal expansion. The low-melting

glass powder comprises amorphous glass comprising mainly V_2O_5 and contains P_2O_5 and Sb_2O_3 and has a distortion temperature (viscosity: 10^{11} P) below 400°C and thermal expansion coefficient of 90 x 10^{-7}/°C or lower. On the other hand, the low-thermal-expansion powder is one or more chosen from β-eucryptite, β-spodumene, cordierite, quartz glass, lead titanate, $NaZr_2(PO_4)_3$, $CaZr_2(PO_4)_3$, and $KZr_2(PO_4)_3$.

Also, the present invention concerns ceramic packages sealed with the sealants described above.

Next, the present invention is explained in detail. As described above, in the present invention, low-melting glass powder from mainly V_2O_5-based amorphous glass containing P_2O_5 and Sb_2O_3 and having distortion temperature (viscosity: 10^{11} P) below 400°C and thermal expansion coefficient of 90 x 10^{-7}/°C or lower is mixed with 50 vol.% or less (in total volume) of low-thermal-expansion powder with particle diameter 50 μm or smaller and thermal expansion coefficient 20 x 10^{-7}/°C or lower and chosen from β-eucryptite, etc., to obtain sealants with thermal expansion coefficients of 45 x 10^{-7}/°C or lower and sealing temperature of 500°C or lower.

The sealants of the present invention are effective for sealing ceramic packages, especially LSI packages, and for such sealing, electrically insulating SiC, Si, mullite, AlN, etc., are used for the package substrates of LSI packages.

Next, the present invention is explained in further detail.

First, as a result of various investigations in terms of low-temperature sealing, low thermal expansion, etc., it was discovered that mainly V_2O_5-based amorphous glass containing P_2O_5 and Sb_2O_3 is suitable for substrate glass of sealants.

Next, the low-thermal-expansion material needed for reducing thermal expansion (hereafter referred to as fillers) was investigated in terms of type, particle size, weight ratio, etc. To satisfy the thermal expansion coefficient requirements of 45 x 10^{-7}/°C or lower needed for sealants, fillers with thermal expansion coefficients of 20 x 10^{-7}/°C or lower are desired. The volume percentage of the fillers in the sealing material should be 50 vol% or less. Also, for maintaining the low thermal expansion properties of sealants, it was learned that a filler particle diameter of 50 μm or smaller is suitable. As a result of an investigation of fillers capable of inhibiting reaction with substrate glass, it was learned that most suitable fillers used with mainly V_2O_5-based substrate glass should be one or more chosen from β-eucryptite, β-spodumene, cordierite, quartz glass, lead titanate, $NaZr_2(PO_4)_3$, $CaZr_2(PO_4)_3$, and $KZr_2(PO_4)_3$, which have also been used in sealants using conventional $PbO-B_2O_3$ glass as the substrate glass.

The mainly V_2O_5-based low-melting glass may be the water-resistant low-melting glass composition disclosed in Japanese Kokai Patent Application No. Sho 62[1987]-78128 with V_2O_5 content 55-70 wt%, P_2O_5 content 17-30 wt% and Sb_2O_3 content 2-20 wt%. Such a glass

composition may have a PbO content of 20 wt% or less, TiO_2 content of 15 wt% or less and/or Na_2O_3 content of 5 wt% or less.

By using the above sealants from mainly V_2O_5-based low-melting glass mixed with fillers, highly reliable low-temperature-sealable LSI packages with low thermal expansion and good airtightness can be obtained.

Operation

The Si semiconductors fitted in LSI packages have a thermal expansion coefficient about 35 x 10^{-7}/°C; thus, the ceramic substrates and sealants should have thermal expansion coefficients comparable to those of semiconductors for prevention of semiconductor cracks occurring during bonding and sealing and also prevention of package leaks caused by sealant cracks. Very low package sealing temperature is desired to prevent deteriorating reliability of Si semiconductor performance.

The thermal expansion coefficient or 45 x 10^{-7}/°C or lower of sealants is close to the thermal expansion coefficient of Si semiconductors and low-thermal-expansion ceramics loaded on the LSI packages so as to reduce thermal stress exerted to the semiconductor as much as possible. For maintaining the sealant thermal expansion coefficient at 45 x 10^{7}/°C or lower, it is necessary to reduce the thermal expansion coefficient of the substrate glass of the sealant to 90 x 10^{-7}/°C or lower and thermal expansion coefficient of the low-thermal-expansion material (filler) to 20 x 10^{-7}/°C or lower.

Thus, the mainly V_2O_5-based amorphous glass containing P_2O_5 and Sb_2O_3 disclosed in the above Japanese Kokai Patent Application No. Sho 62[1987]-78128 for low thermal expansion properties is selected for the substrate glass. With this selection, low thermal expansion and also low working temperature as with the conventional PbO-B_2O_3 type amorphous glass are possible, giving various properties such as high strength, high water resistance, etc., and high glass flowability needed for airtight sealing of packages.

Next, in terms of vol%, the filler content in the sealants should be 50 vol% or less. With filler content above 50 vol%, the substrate glass flowability effect is lost, resulting in poor sealing of the packages. The filler particle diameter should be 50 μm or smaller. With the filler particle diameter above 50 μm, due to the thermal expansion difference with the substrate glass, cracks occur at the interface between the substrate glass and filler, making airtight sealing of the packages difficult.

The fillers should be one or more chosen from β-eucryptite, β-spodumene, cordierite, quartz glass, lead titanate, $NaZr_2(PO_4)_3$, $CaZr_2(PO_4)_3$, and $KZr_2(PO_4)_3$, for the filler thermal expansion coefficient to be 20 x 10^{-7}/°C or lower and for improved adhesive strength by inhibiting the reaction with the V_2O_5-based substrate glass.

The sealants should have a sealing temperature of 500°C or lower and substrate glass distortion temperature of 400°C for heat resistance of Si semiconductors of LSI packages.

Application examples

Next, the present invention is explained in further detail with examples, while the present invention is not limited to such examples.

Application Example 1

A method for the preparation of a sealant of the present invention is described.

First, various oxide starting materials needed for making mainly V_2O_5-based substrate glass were compounded, weighed, mixed, melted in an alumina crucible in an electric furnace at 1000-1100°C for 1-2 h, cast into a plate form and pulverized in a mortar to a particle diameter of 50 μm or smaller, then ball-milled to 10 μm or smaller to obtain substrate glass powder. Next, this powder was mixed with the low-thermal-expansion filler of a particle diameter 50 μm or smaller in a desired amount and mixed in a mixer to obtain sealants of the present invention.

Table 1 shows compositions, distortion temperatures and thermal expansion coefficients of substrate glass of the sealants obtained above. In Table 1, the V_2O_5-P_2O_5-Sb_2O_3 substrate glass used in samples A-1~7 in examples of the present invention is a low-melting glass with distortion point of 400°C or lower with thermal expansion coefficient of 90 x 10^{-7}/°C or lower and had a lower thermal expansion than the PbO-B_2O_3 glass of Sample Nos. B-1 and B-2. Here, the thermal expansion coefficient is in the range of 50°C to the glass transition temperature.

Table 2 shows the compositions and various properties of sealants of the present invention obtained by mixing low-thermal-expansion filler with the substrate glass of mainly V_2O_5-P_2O_5-Sb_2O_3 as the main component as shown in Table 1. In Table 2, the substrate glass of A-2, A-3 and A-5 with V_2O_5-P_2O_5-Sb_2O_3 as the main component shown in Table 1 was mixed with the low-thermal-expansion material in the vol% shown in the table. The thermal expansion coefficient was measured between 50°C and the glass transition temperature for a hot-molded rod of diameter 5 mm. For flowability, after press molding to a diameter of 10 mm and a thickness of 5 mm, the diameter was measured for the molding (flow button) when heated 10 min at the seal temperature shown in the table. The bending strength was measured by a 4-point bending test for a hot-molded angular rod of a width of 4 mm, thickness 5 mm and length 40 mm. Sample Nos. C-1~8 are for the application examples of the present invention and D-1 and D-2 are for comparative examples using conventional substrate glass of PbO-B_2O_3 as the main component.

The sealants of the present invention as shown in Table 2 have a sealing temperature of 500°C or lower, enabling low-temperature sealing and have a thermal expansion coefficient of

45 x 10^{-7}/°C or lower, lower than conventional sealants. Also, the flowability is comparable or superior to conventional sealants. Furthermore, the bending strength is 1.6-2.0 times that of conventional sealants. Thus, by using sealants containing substrate glass of V_2O_5-P_2O_5-Sb_2O_3 as the main components of the present invention for package sealing, the thermal expansion coefficient is similar to that of Si semiconductors mounted on the packages, resulting in reduced thermal stress exerted on the semiconductor and enhanced sealing strength, the preventing cracks.

Table 1

1 試料No		2 組成(重量%)					3 変形点	熱膨張係数 4
		V_2O_5	P_2O_5	Sb_2O_3	PbO	Tl_2O	(℃)	(×10^{-7}/℃)
5 実施例	A－1	50	25	10	15		377	78
	A－2	50	25	20	5		375	70
	A－3	55	25	10	10		369	80
	A－4	55	25	10	6	4	370	80
	A－5	60	20	10	5	5	330	84
	A－6	60	20	10	10		333	85
	A－7	60	20	7	7	6	329	65
6 比較例	B－1	85PbO-13B_2O_3-1SiO_2-1Al_2O_3					322	115
	B－2	80PbO-13B_2O_3-2SiO_2-3ZnO-3Al_2O_3					345	110

Key:
1 Sample No.
2 Composition (wt%)
3 Distortion point
4 Thermal expansion coefficient
5 Application Example
6 Comparative Example

Table 2

1 試料No		2 ースガラス	3 低熱膨張材 (体積%)	4 着温度 (℃)	5 膨張係数 (×10⁻⁷/℃)	6 動性 (mm)	7 げ強度 (MPa)
8 実施例	C－1	A－2	β－ユークリプタイト (30%) 10	450	28	15	51
	C－2	A－2	β－スポジューメン (48%)	450	40	15	50
	C－3	A－3	チタン酸鉛 (30%)	440	42	14	45
	C－4	A－2	コージェライト (50%)	440	44	14.5	49
	C－5	A－5	β－ユークリプタイト (20%)	430	45	15	46
	C－6	A－5	β－ユークリプタイト (50%)	430	41	15	47
	C－7	A－5	チタン酸鉛 (37%)	430	42	15.5	47
	C－8	A－5	チタン酸鉛 (45%)	430	37	15	48
9 比較例	D－1	B－1	チタン酸鉛 (40%)	430	55	15	25
	D－2	B－2	チタン酸鉛 (35%)	430	60	14.5	30

Key:
1 Sample No
2 Substrate glass
3 Low-thermal-expansion material (vol%)
4 Sealing temperature
5 Thermal expansion coefficient
6 Flowability
7 Bending strength
8 Application Example
9 Comparative Example
10 β-Eucryptite
β-Spodumene
Lead titanate
Cordierite
β-Eucryptite
β-Eucryptite
Lead titanate
Lead titanate
Lead titanate
Lead titanate

Application Example 2

Figure 1 shows a cross-sectional diagram of an LSI package using the sealant of the present invention. Figure 1 shows heat sink fin 1, silicone rubber 2, lead frame 3, package cap 4,

LSI (Si semiconductor) 5, adhesive 6, sealant 7 and package substrate 8. LSI 5 is sealed with the sealant 7 by the package substrate 8 and the package cap 4.

Table 3 shows thermal cycle test results measured for the life of LSI packages using the sealants and low-thermal-expansion ceramic substrate shown in Table 2. The thermal cycle test was carried out in the temperature range -55~150°C. In a number of cycles, He leakage of 5 x 10^{-10} atm-cc/°C or less was considered passing. For inhibition of effects of thermal stress to semiconductors, the substrate used in the tests of Table 3 was SiC having a thermal expansion coefficient 37 x 10^{-7}/°C and a low thermal expansion comparable to that of semiconductors.

As shown in the table, the packages E-1~3 using the sealants C-1, C-6 and C-8 of the present invention shows thermal cycles 2000 cycles or more, clearly more than 2 times the package G-1 using conventional sealant D-1. Excellent thermal cycle characteristics were also confirmed even when low-thermal-expansion substrates such as Si, mullite and AlN, similarly to the SiC substrate.

Table 3

1 試料No		2 封着材料	3 熱サイクル試験 (回)
4 実施例	E-1	C-1	≥ 2000
	E-2	C-6	≥ 2000
	E-3	C-8	≥ 2000
5 従来	G-1	D-2	800

Thermal cycle test: -55~150°C

Key:
1 Sample No.
2 Sealant
3 Thermal cycle test
4 Application Example
5 Conventional

Effect of the invention

According to the present invention, sealants with excellent flowability affording good workability at low temperature, high strength and low thermal expansion can be obtained. By combining these sealants with package substrates with low thermal expansion, LSI packages with excellent reliability with good airtightness and thermal cycle properties can be obtained.

<u>Brief description of the figure</u>

Figure 1 is a cross-sectional diagram of an LSI package using the sealant of the present invention.

4 Package cap
5 LSI (Si semiconductor)
7 Sealant
8 Package substrate

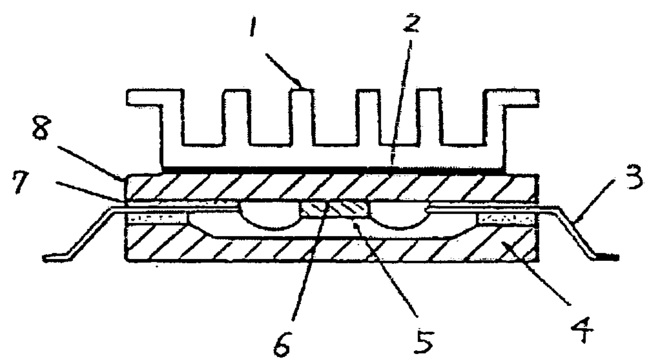

Figure 1